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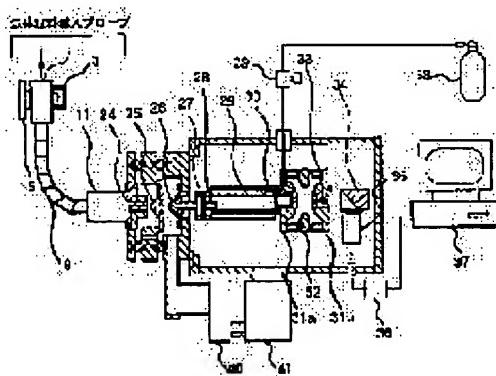
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(54) ANALYSIS DEVICE

(57) Abstract:

PROBLEM TO BE SOLVED: To easily and sensitively measure dioxin, organic nitro compound, or the like by introducing a gas sample to be measured to a gas sample introduction part and performing the mass spectrometry of an ion being generated due to the corona discharge of the introduced gas sample.

SOLUTION: When a gas sample is to be introduced from a gas sample introduction port 1 using a gas introduction pump 11, a grip, a probe tip heating heater, a filter, a dust take-out port, and the like are preferably provided at the tip of the gas sample probe. Also, the heater is wound around the gas sample introduction pipe 8, thus increasing the temperature of the sample. With this configuration, a sample that is introduced via the gas sample introduction probe enters the corona discharge part for performing corona discharge. A negative ion being generated here passes through first, second, and third pores 24, 25, and 26, a static electricity lens 27, a slit 28, a deflector 29, a gate electrode 30, and the like and is introduced to an ion trap type mass spectrograph with an end cap electrode 31a, a ring electrode 32, and the like for performing a specific mass spectrometry.



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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[The technical field to which invention belongs] This invention relates to the analysis apparatus [it is suitable especially to analyze in detail the deadly poison dioxin generated from an incineration facility etc. about an analysis apparatus, and] which can also measure the steam evaporated from the dangerous substance, such as the explosive substance represented by the nitro compound, and the agricultural chemicals containing chlorine or the Lynn element.

[0002]

[Description of the Prior Art] The method by the gas chromatograph-mass spectrometer using the magnetic field mold mass spectrometer of a high resolution as conventional technology for analyzing dioxin is learned. This method is the method of irradiating an electron ray, using dioxin as positive ion, and detecting with the magnetic field mold mass spectrometer of a high resolution, after introducing into a gas chromatograph the dioxin mixture condensed through the complicated pretreatment process and dissociating. This method has the feature it not only can perform qualitative analysis (the class of dioxin [have / whether it is dioxin which chlorine combined how many, / it / a dibenzo PARAJI oxine or a dibenzofuran frame] is got to know) of dioxin from the mass number of the detected ion, but that it can perform quantitative analysis of dioxin from the reinforcement of the detected ion.

[0003] On the other hand, the method shown in drawing 18 is indicated by organic mass spectrometry (Organic Massspectrometry), 16 volumes, and 275 - 278 pages as one of the conventional technology in dangerous-substance detection equipment. Nitrogen etc. carries out gas passage, and this method carries out the fuel spray of the dinitrobenzene which melted into solvents, such as a methanol, to the pipe 55 in which it was prepared in through at the capillary 54, and was prepared by this capillary 54 at the same axle, and makes a drop 58 generate in large quantities. At this time, the generated drop 58 is made detailed by the heating tube 56 heated at the heating-tube heater 57, and a part evaporates it. Then, the vaporized molecule is introduced into the negative corona discharge field by the needle electrode 59 for corona discharge, and the negative ion about a sample molecule generates it by electron attachment or the ion molecular reaction.

[0004] The generated ion is introduced into the mass analysis section 60 which consisted of quadrupole mass spectrometers which exist in a high vacuum through pore, and is detected. The amount of the dangerous substance can be presumed from the reinforcement of the ion which could presume what kind of the dangerous substance there is from the mass number of the detected ion like the method by the above-mentioned gas chromatograph-mass spectrometer, and was detected also by this method.

[0005]

[Problem(s) to be Solved by the Invention] In the dioxin analysis using the above-mentioned conventional high-resolution magnetic field mold mass spectrometer, it was analyzing by just ionizing dioxin by the exposure of an electron ray. However, since this method did not have the sufficiently high generation effectiveness of the cation from a dioxin molecule, its detection sensitivity was low, therefore before it analyzed, it needed to perform complicated pretreatment and needed to condense dioxin for the high scale factor. Moreover, it was complicated, and since pretreatment which requires a long time was necessity, there was a problem that time amount and analysis cost also started.

[0006] On the other hand, since the above-mentioned conventional dangerous-substance detection

equipment had the low ion generation effectiveness of the nitro compound in the ion source, when the amount of a sample was a minute amount, it not only cannot carry out the direct method of analysis of the steam of a solid sample, but [since the solid sample is melted and introduced into solvents, such as a methanol,] it had the defect that detection was difficult.

[0007]

[Means for Solving the Problem] In order to solve a problem of the above-mentioned conventional technology, an analysis apparatus of this invention has the mass analysis section which carries out mass analysis of the ion which produced the above-mentioned gaseous sample introduced with sample induction which introduces a gaseous sample which should be measured by the negative corona discharge section which carries out corona discharge and the negative above-mentioned corona discharge.

[0008] That is, according to this invention, using a property in which the dangerous substance represented by dioxin which is a kind of an organochlorine compound, and nitro compound tends to become negative ion, it is ionized using negative corona discharge and generated negative ion is measured by mass spectrometer. Since generation effectiveness of an anion by negative corona discharge is farther [than generation effectiveness of a cation] high, complicated pretreatment [like / detection sensitivity is also sufficiently high, therefore / the above-mentioned conventional technology] it is unnecessary.

[0009] The above-mentioned sample induction has a heating unit for heating the above-mentioned gaseous sample to a predetermined temperature.

[0010] That is, in order for negative corona discharge to generate an anion efficiently, it is effective that make into an elevated temperature temperature of a gaseous sample introduced into the ion source, or a needle electrode for corona discharge is heated. Moisture of a gaseous sample introduced as a gaseous sample is a more than elevated temperature, for example, 100 degrees C, is also evaporated, and ionization by corona discharge is efficiently carried out to stability. Moreover, since corona discharge starting potential falls, high corona discharge current is acquired also on the same corona discharge voltage and generation effectiveness of ion will rise if temperature of a needle electrode goes up, it is effective to prepare a heating unit and to raise temperature of a gaseous sample.

[0011] This heating unit is arranged at the preceding paragraph of a gaseous sample installation pump for introducing the above-mentioned gaseous sample, it has dual structure which consists of an inner tube along which the above-mentioned gaseous sample passes, and an outer tube arranged on the outside of the inner tube concerned, and a heater for heating the above-mentioned gaseous sample may be made to be arranged between inner tubes and outer tubes concerned. Moreover, it has dual structure which consists of an inner tube with which it is arranged at the preceding paragraph of a gaseous sample installation pump for introducing the above-mentioned gaseous sample, and the above-mentioned gaseous sample passes along the above-mentioned heating unit, and an outer tube arranged on the outside of the inner tube concerned, and a heater for heating the above-mentioned gaseous sample may be made to be arranged inside the inner tube concerned.

[0012] Moreover, heating of the above-mentioned gaseous sample may be made to be performed by heater arranged so that the above-mentioned heating unit may be arranged to that between a gaseous sample installation pump for introducing the above-mentioned gaseous sample, and the above-mentioned corona discharge section and the introduced above-mentioned gaseous sample may be touched.

[0013] Mass analysis of the ion generated in the above-mentioned corona discharge section is introduced and carried out to the above-mentioned mass analysis section through pore prepared between the above-mentioned corona discharge section and the above-mentioned mass analysis section.

[0014] A device which controls a pressure of the corona discharge circles concerned to a desired pressure can be prepared in the above-mentioned corona discharge section. Therefore, an outlet for taking out surplus gas of the corona discharge circles concerned to the exterior can be established in the above-mentioned corona discharge section, light weight is formed in the outlet concerned, and a discharge of surplus gas may be made to be controlled automatically, and may prepare a bulb for gases in the above-mentioned bulb.

[0015] A means to heat the above-mentioned corona discharge section is established, and if it is made to

carry out corona discharge of the sample maintained at high temperature, a result desirable as mentioned above will be obtained.

[0016] If an ion trap mold mass spectrometer is used as the above-mentioned mass spectrometer, since very high sensitivity will be obtained and complicated pretreatment by the above-mentioned gas chromatograph will become unnecessary, it is very desirable.

[0017] Furthermore, although a discharge field by corona discharge is atmospheric pressure mostly, it can usually make high ion generation effectiveness in a corona discharge field by changing this field into a sealing condition and raising molecule density in a corona discharge field.

[0018]

[Embodiment of the Invention] According to this invention, the detection and the quantum of organic nitro compounds, such as an organic compound, which have the dioxin (organic compound which has the dioxin from which the number of chlorine differs, dibenzo parao KISHIN containing chlorine, and a dibenzofuran frame) and three nitro groups or more which are organochlorine compounds can be performed. Therefore, it cannot be overemphasized that this invention can be applied not only to dioxin but to the agricultural-chemicals analysis apparatus which detects agricultural chemicals including chlorine or Lynn.

[0019] The above-mentioned organochlorine compound and an organic nitro compound tend to become negative ion, and negative ion is easily generated by negative corona discharge. Since ion positive [instead of negative] was used conventionally, detection sensitivity was low, therefore complicated, and after condensing the measuring object by pretreatment by the gas chromatograph which requires long duration, mass analysis of high sensitivity needed to be performed.

[0020] However, in this invention, since negative ion is formed of negative corona discharge and IONGA measurement of negative [this] is carried out, sensitivity higher than the case of the above-mentioned former which used positive ion for measurement is obtained. And like dioxin, since high scale-factor concentration of a sample can be performed by using the ion trap mold mass spectrometer which can save up ion inside as a mass spectrometer, even when the concentration of the measuring object is very low (0.1 or less ppt), analysis can be ensured and it is the most desirable. However, it is also possible to use a quadrupole mold mass spectrometer and a magnetic field mold mass spectrometer.

[0021]

[Example] <Example 1> Drawing 1 is drawing showing the configuration of the analysis apparatus of the 1st example of this invention. Although it is effective practically to precede to perform negative corona discharge in this invention like a postscript, and to heat a sample, this example is an example which heated the sample with the gaseous sample installation probe formed in the preceding paragraph of the gaseous sample installation pump 11.

[0022] Two examples of this gaseous sample installation probe were shown in drawing 2 and drawing 3, respectively. First, the case of drawing 2 is explained. As a gaseous sample installation pump 11 for introducing a gaseous sample from the gaseous sample inlet 1, the introductory flow rate used the gas installation pump which has a several l./m to about dozens of l. mechanical device like a diaphragm pump. If it depends to the length of the gaseous sample installation pipe 8 strongly and the gaseous sample installation pipe 8 becomes long, the gaseous sample installation pump 11 with high capacity needs to be used for the capacity of the gaseous sample installation pump 11.

[0023] In order to prevent the adsorption of a gaseous sample to the wall of the gaseous sample installation pipe 8, it is necessary to raise the temperature inside the gaseous sample installation pipe 8 at the time of introducing a gaseous sample. Therefore, a heater 10 is wound around the gaseous sample installation pipe 8, and it enabled it to go up the temperature of a sample, as shown in drawing 2. Usually, temperature of the gaseous sample installation pipe 8 is carried out to beyond a room temperature (10-30 degrees C), and it was made to become about 100-200 degrees C. it is like [in this example / around it] a bellows pipe using a flexible pipe like Teflon as a gaseous sample installation pipe 8 -- although it was hard, the bendable pipe 9 was formed, and the gaseous sample installation pipe 8 was reinforced mechanically.

[0024] When introducing a gaseous sample using the gaseous sample installation pump 11, in order to make it easy to have by hand, a handle 3 can be formed at the tip of a gaseous sample installation probe,

or the switch 2 of the gaseous sample installation pump 11 can also be formed in it near the handle 3. The end-of-the-probe heating heater 4 is formed, and in order to prevent adsorption of the gaseous sample for the point of a gaseous sample installation probe or to prevent attracting a big particle and dust in the gaseous sample installation pipe 11, a filter 6 can also be formed at the tip of a gaseous sample installation probe. In this case, it is desirable to form the dust output port 7 for taking out the dust by which the filter 6 was adsorbed.

[0025] Furthermore, since steams, such as dioxin, occur [the direction which the solid sample was heated / direction / and generated the steam] and detection becomes easy when measuring the dioxin in a solid sample etc., it is useful practically to form the heating units 5, such as an infrared lamp and a halogen lamp.

[0026] On the other hand, with the structure shown in drawing 2, since a heater 10 also becomes so long when the length of the gaseous sample installation pipe 8 exceeds several m, a price rises. Then, as shown in drawing 3, metal wire heater 12a wound around multiplex is prepared in the gaseous sample installation pipe 8, and the gaseous sample to pass was heated directly. Two or more metal wire heaters 12a and 12b may be used, and when the gaseous sample installation pipe 8 is long, the number can also be made to increase further, as shown in drawing 3. In case it is actually used, after starting suction of a gaseous sample with the gaseous sample installation pump 11, energization heating of the metal wire heater 12 is started, and measurement is started after fixed time amount by which the metal wire heater 12 was fully heated.

[0027] By making it such a sequence, the problem of a gas-like sample with a low temperature sticking to the wall of the gaseous sample installation pipe 8 is also mitigated. Moreover, since what is necessary is just to arrange the metal wire heater 12 for every fixed distance of a certain even when using the long gaseous sample installation pipe 8, the rises of a price are also few. Moreover, since it is energization heating, since the temperature of a metal wire heater rises to a temperature predetermined in a short time for about several seconds, it does not always need to heat the metal wire heater 12, and operation cost is also low [temperature]. Furthermore, if the metal wire heater 12 heated by the elevated temperature is arranged just behind the gaseous sample inlet 1, since the particle containing moisture will also be heated and it will evaporate, installation of the big particle containing such moisture is prevented. As shown in drawing 2, a filter 6 and dust output port 7 may be formed.

[0028] The sample introduced through the gaseous sample installation probe The negative ion which went into the corona discharge section (illustration is omitted by drawing 1) for performing negative corona discharge, and was generated here It is introduced into the ion trap mold mass spectrometer which has end cap electrode 31a, the ring electrode 32, etc. through the 1st, 2nd, and 3rd pores 24, 25, and 26, an electrostatic lens 27, a slit 28, deflecting system 29, the gate electrode 30, etc., and predetermined mass analysis is performed.

[0029] <Example 2> This example is an example prepared in the latter part of the sample installation pump 11, and explains a sample heating unit using drawing 4 -9. The gaseous sample which should be measured is introduced in the gaseous sample heating furnace 13 from the gaseous sample installation pipe 8 with the gaseous sample installation pump 11. The gaseous sample to which the insulating pipe 14 made from the quality of the material with which this gaseous sample heating furnace 13 bears an elevated temperature like a quartz into a metal block passes through this field at the metal wire heater 15 which was formed and was placed into it is heated by the elevated temperature. What wound metal wires, such as a nichrome wire, around multiplex as a metal wire heater 15 was used. Although the path of an insulating pipe is dependent also on the flowing quantity of gas, it is about 5mm in the case where a gas about 21./m is introduced. The length of the insulating pipe 14 was set to about 10cm. Instead of the above-mentioned metal wire heater 15, as shown in drawing 5, the collision board heating heater 42 is formed, and a gaseous sample may be made to collide with two or more of these heated collision boards 43, and may be heated.

[0030] Thus, if a sample is heated, even if a particle is introduced, since it is prevented that collide and evaporate at the metal wire heater 15 or the collision board heating heater 42, and a particle, moisture, etc. introduce into a corona discharge field directly, corona discharge will not become unstable. This metal wire heater 15 is controlled by the metal wire heater heating power supply 16 by desired temperature, and the temperature of this field is kept at about 50 to 400 degrees C.

[0031] The gaseous sample which passed the sample heater 13 is introduced into the corona discharge section 17, and negative is ionized. It was made for the tip of the introductory path 18 of a gaseous sample to be located near the needle electrode 21 for corona discharge so that the introduced gaseous sample may be efficiently sent to the corona discharge field at needle-electrode 21 tip for corona discharge.

[0032] As the above-mentioned introductory path 18, as shown in drawing 6, the path at a tip may use the small introductory path 45. For example, when setting the bore of the path to the middle to about 5mm and setting the bore at a tip to about 1mm, the introduced gaseous sample has been introduced into the corona discharge field at needle-electrode 21 tip for corona discharge certainly and efficiently. At this time, the length of the gaseous sample installation path 18 was set to about 5cm. The about 21 needle electrode [for corona discharge] introductory path 18 was made into products made from an insulating material, such as Teflon, MAKORU glass, and a ceramic, so that the electric field in needle-electrode 21 tip for corona discharge might not be weakened. This field can also be heated at the corona discharge section heating heater 19 as well as the gaseous sample heating furnace 13. Usually, the temperature of this field is kept at about 50 to 300 degrees C by the corona discharge section heating heater power supply 20.

[0033] The needle electrode 21 for corona discharge is formed in the corona discharge section 17, and it enabled it to impress the negative high voltage (about -2 to -5kV) to it according to the power supply 22 for corona discharge. Distance with the surrounding counterelectrode 17 was set to about several mm.

[0034] Although the sample introduced through the 1st pore 24 from the corona discharge section 17 is sent to a mass spectrometer through the 2nd pore 25, surplus gas other than ion or a molecule is discharged from the surplus gas outlet 23 outside.

[0035] The total current value acquired by the corona discharge in when not heating with the case (150 degrees C) where the gaseous sample in the gaseous sample heating furnace 13 is heated (30 degrees C) was shown in drawing 8. The chlorobenzene was used as a sample and the steam from the sample of a room temperature was attracted with the gaseous sample suction pump 11.

[0036] When it was heated that corona discharge voltage is also the same (-2.5kV) and the direction of (a) did not heat so that clearly from drawing 8, the current value increased about 2.5 times from (b). And the direction at the time of also heating the stability of current was far good. The moisture of the gas-like sample introduced as the temperature of a gaseous sample is a more than elevated temperature, for example, 100 degrees C, was also evaporated, and ionization by corona discharge was efficiently carried out to stability. Moreover, when the temperature of the needle electrode 21 for corona discharge rose indirectly, corona discharge starting potential fell, and since high corona discharge current was acquired by the gaseous sample heated by the elevated temperature even if discharge voltage is the same, the generation effectiveness of ion also rose by it.

[0037] It was admitted that not only temperature but the pressure of the field where ion is generated by corona discharge was important. Usually, the surplus gas outlet 23 for taking out the surplus gas which does not flow from the pore which incorporates ion in a vacuum with the atmospheric pressure ion source which uses corona discharge out of the ion source is formed. Therefore, this surplus gas outlet 23 is always in an open condition, and the corona discharge field has atmospheric pressure (760Torr degree) mostly. However, in fact, the one more than atmospheric pressure where the molecule density in a corona discharge field is higher became high, and its ionization efficiency was [the optimum value of the pressure of a corona discharge field] higher than 760Torr(s) of atmospheric pressure.

[0038] On the other hand, if the pressure in the pore 25 (diameter of about 0.2-0.5mm) neighborhood which incorporates ion in the vacuum of a mass spectrometer is too high, the number of the molecules which flow into the mass analysis section under a high vacuum through this pore 25 will increase too much, and it will become difficult to maintain the mass analysis section to a high vacuum. The surplus gas outlet 23 shown in drawing 4 was taken up, with the gaseous sample installation pump 11, a gas is introduced continuously and the pressure inside the corona discharge section 17 was heightened there. However, when the light weight 46 for reducing conductance to a surplus gas outlet is placed and the pressure of the corona discharge section 17 interior became high too much as shown in drawing 7 (a) since there was too much inflow of the gas from the 1st pore 24 for incorporating ion in a vacuum the way things stand, weight 46 floats and it was made for surplus gas to come out to the exterior from a

surplus gas outlet. Thereby, the pressure of the corona discharge section 17 was controllable by the relation between the quantity of gas which flows into the corona discharge section 17, and the weight of weight 46 to the desired value. Moreover, this bulb 47 for gases may be opened and closed periodically, and as shown in drawing 7 (b), while the bulb 47 for gases is formed in the place of a surplus gas outlet and the gaseous sample installation pump 11 is operating instead of weight 46, the pressure of a corona discharge field may be controlled.

[0039] The above-mentioned weight 46 was put on the surplus gas outlet, and the result of having compared the case (open condition) where made open the time dependency (sealing condition) and the surplus gas outlet of a current value at the time of making the pressure of a corona discharge field high, and it measured under atmospheric pressure mostly was shown in drawing 9. The peak acquired by attracting the steam from the sample in a room temperature with the gaseous sample suction pump 11 was compared using a chlorobenzene as a sample. Consequently, it was admitted that sensitivity was higher than the case where former one is the latter, about 3 times, and it was effective in the rise of sensitivity to make high the pressure of the corona discharge section 17 interior so that clearly from drawing 9.

[0040] <Example 3> Although various mass spectrometers can be used in order to analyze the ion generated in the corona discharge section 17, the case where the ion trap mass spectrometer of an ion reservoir lump mold is used is explained using drawing 1. It is the same even when other mass spectrometers, such as a quadrupole mass spectrometer and a magnetic field mold mass spectrometer, are used.

[0041] The ion generated in the corona discharge section (drawing 1 is not shown) The 1st pore 24 (the diameter of about 0.3mm) of the differential-pumping section heated at the heater 19 In the course which passes a length of about 20mm, the 2nd pore 25 (the diameter of about 0.2mm, a length of about 0.5mm), and the 3rd pore 26 (the diameter of about 0.3mm, a length of about 0.5mm) By heating, the collision with a neutral molecule, etc., the cleavage of cluster ion happens and the ion of a sample molecule generates. Moreover, cleavage of a cluster is performed by the collision with the molecule which remains at the same time it can impress voltage now between the 1st pore 24, the 2nd pore 25 and the 2nd pore 25, and the 3rd pore 26 and raises ion permeability.

[0042] The differential-pumping section is usually exhausted by the roughing vacuum pumps 40, such as a rotary pump, a scrolling pump, or a mechanical booster pump. A turbo molecular pump can also be used for exhaust air of this field. The pressure between the 2nd pore 25 and the 3rd pore 26 was set to 0.1 - 10Torr. After the generated ion passes the 3rd pore 26, it converges it with an electrostatic lens 27. As this electrostatic lens 27, the AINTSUERU lens which consists of an electrode of three sheets was used.

[0043] After ion passes a slit 28, it is deflected with deflecting system 29 and introduced into the ion trap mass spectrometer which consists of bowl-like the end cap electrodes 31a and 31b and the ring electrode 32 of a pair through the gate electrode 30. A slit 28 restricts the solid angle of the jet containing the neutral particle which flows from a skimmer, and prevents introducing an unnecessary particle etc. in an ion trap mass spectrometer. Deflecting system 29 was formed in order that the neutral particle which passed the skimmer might prevent being introduced into the direct ion trap mass analysis section through the pore of end cap electrode 31a. In this example, it deviated using the electric field of the outer case which oozed out from opening of a container liner using the duplex cylindrical deflecting system 29 which consists of the container liner and outer case with which much openings were prepared. In case the gate electrode 30 takes out the ion saved up to ion trap mass analysis circles out of a system, it carries out the duty which prevents that ion is introduced into mass analysis circles from the exterior.

[0044] After it collides with gas, such as helium introduced into ion trap mass analysis circles, and that orbit becomes small, by scanning the RF electric field impressed to the ring electrode 32, the ion introduced into these ion trap mass analysis circles is discharged out of a system, and is detected by the ion detector through the drawer lens 33. Gas, such as helium, is supplied through a regulator 39 from sources of supply, such as a bomb 38. Since one of the advantages of an ion trap mass spectrometer has the property of saving up ion, even when the concentration of a sample is thin, if the time amount to save up is developed, it will be a detectable point. Therefore, like dioxin analysis, since high scale-factor concentration of ion is possible in the ion trap mass analysis section even when sample concentration is

low, pretreatment of a sample can be facilitated. In detection of the ion taken out from the ion trap mass analysis section, ion is changed into an electron by the conversion dynode 34, and a scintillation counter 35 detects the electron. After amplifying the acquired signal with amplifier 36, it is sent to a data processor 37.

[0045] The chamber by which an electrostatic lens 27, a slit 28, deflecting system 29, the gate electrode 30, the ion trap mass analysis section, and an ion detector have been arranged is exhausted with a turbo molecular pump 41. In addition, although an auxiliary pump is needed for a turbo molecular pump 41 at a back pressure side, it is possible to use also [roughing vacuum pump / 40 / which uses this for the differential-pumping section]. In this example, the about 200l. [/second] turbo molecular pump was used for the differential-pumping section for the scrolling pump with a displacement of about 900l. [/minute] as the exhaust for chambers, and the scrolling pump was also [section] used as an auxiliary pump of this turbo molecular pump. By making it such a system, the exhaust air system of the atmospheric-pressure-ionization-mass-spectrometry equipment which tends to become complicated was able to be simplified extremely. In addition, although deflecting system 26 was used in this example, it is possible also when not deflecting ion.

[0046] Usually, in a data processor 37, time amount change (mass chromatogram) of the relation between the mass number/charge, and ionic strength (mass spectrum) and the ionic strength of a certain mass number/charge etc. is displayed. 1, 2, and 3 trichlorobenzene was shown in drawing 10 , and the example of mass-spectrum measurement of 1, 2, and 3 TORIKURORO dibenzo PARAJI oxine (a kind of dioxin) was shown in drawing 11 , respectively. In any case, molecular ion M- to which the electron adhered is observed strongly, and it turns out that it is effective in this invention measuring such material. In addition, the molecular structure of 1, 2, and 3 trichlorobenzene and 1 and 2, and 3 TORIKURORO dibenzo PARAJI oxine was shown in drawing 10 and 11. That in which one oxygen was desorbed from the frame of a dibenzo PARAJI oxine is called a dibenzofuran, and its toxicity is strong like a dibenzo PARAJI oxine. This material has also been measured by high sensitivity by this invention. In addition, what saw the molecular ion field of 1, 2, and 3 TORIKUROROBENZOPARAJI oxine observed in details was shown in drawing 19 . It is a complicated peak group originating in two stable isotopes (it is the thing of the mass numbers 34.9688527 and 36.965903, and the abundance ratio is 75.77% and 24.23%, respectively) of chlorine so that a left actual measurement may show. the anion (M-) which generated this peak group by electronic addition which is a main reaction in negative corona discharge -- in addition, that it can explain as superposition of ion (M-H) - generated by dehydrogenation has checked by the comparison of the actual measurement and calculated value which were shown in drawing 19 . On the contrary, quality becomes more certain by employing this feature efficiently by observing the intensity ratio of two or more peaks, for example, the peak of 286 and 288.

[0047] Thus, the organic substance with which the halogen went into the frame of a dibenzo PARAJI oxine and a dibenzofuran tends to become negative ion by negative corona discharge, namely, since the ion generation effectiveness by negative corona discharge is high, it can be measured by high sensitivity by this invention. The example of measurement of the mass chromatogram obtained using 1, 2, and 3 trichlorobenzene as a sample was shown in drawing 12 . Since a measured component will be detected, a signal will go up, if a gaseous sample is introduced into the interior of an analyzer with the gaseous sample installation pump 11, and a signal will disappear if it is made to stop, if this is used, on-line monitoring will become possible.

[0048] Like [the same is said of the case of the nitro compound which poses a problem by detection of the dangerous substance, and] the R dee X shown in the nitrotoluene and the trinitrotoluene which were shown in drawing 13 , and drawing 14 , and PIITIENU, it has three or more nitro groups, and the nitro compound with low vapor pressure has also been measured to high sensitivity. This is because the anion generation effectiveness of the nitro compound by negative corona discharge is high like an organochlorine compound.

[0049] In the case of a nitro compound, when the number of nitro groups increases, there is orientation for the generation effectiveness of an anion to become high. After attracting the steam of the solid sample in a room temperature (20 to 30 degree C) with the gaseous sample installation pump 11 and ionizing this by negative corona discharge, the mass chromatogram which introduced into the mass spectrometer and was detected was shown in drawing 12 and 13. According to this invention, it cannot

be overemphasized that a nitro group can measure one (for example, mono-nitrobenzene shown in drawing 13) or at least two nitro compounds to high sensitivity.

[0050] You may make it a mass spectrum or not a mass chromatogram but the thing simplified further shown for a final display in a data processor 37. That is, case [like dangerous-substance detection equipment], it is also good to indicate whether the nitro compound which poses a problem was detected. For example, when there is a noise level in a certain ion of the specification which should be detected and a signal is detected like drawing 15 more than that level, suppose that this ion was detected. If it is observed beyond a certain fixed time amount in order to distinguish from a mere spike noise at this time, an algorithm which considers that it is a signal will be used. Incorrect actuation can be decreased by adding such an algorithm. At this time, what was shown in drawing 16 as the last display can be used. When the indicator 49 of the material corresponding to a certain ion which should be detected is displayed on the indicator 48 and A is detected by the above-mentioned algorithm, it tells that ** which blinks A, and A were detected. At this time, the concentration of how much, the indicator 50 of the amount which tells (it is good simply for the information on the degree whether there are many amounts or it is few), and alarm 51 may be formed in coincidence.

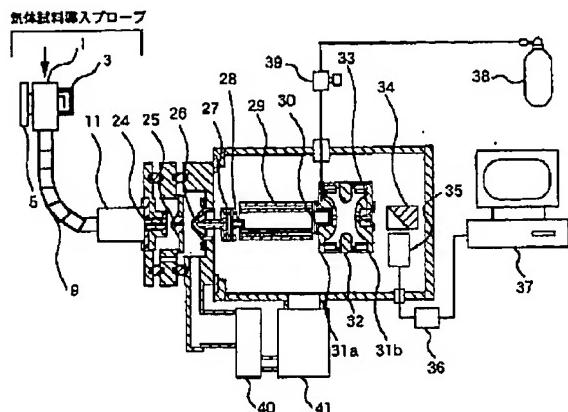
[0051] <Example 4> Although each above-mentioned example showed the case where a gaseous sample was continuously introduced with the gaseous sample installation pump 11, as shown in drawing 17 , it is also possible to introduce a gaseous sample off-line from the gaseous sample installation port 52 by the syringe 53.

[0052] Moreover, -it-is-possible-not-only-a-gaseous-sample but to atomize a solution sample using the atomizer by gas or the atomizer by heating, to introduce this into the gaseous sample heating furnace 13 shown in drawing 2 , and to analyze it, even if it is a solution sample (it may have melted into the organic solvent in dioxin). In this case, since high-speed jet generates from an atomizer, it is not necessary to use a gaseous sample installation pump.

[Translation done.]

Drawing selection drawing 1

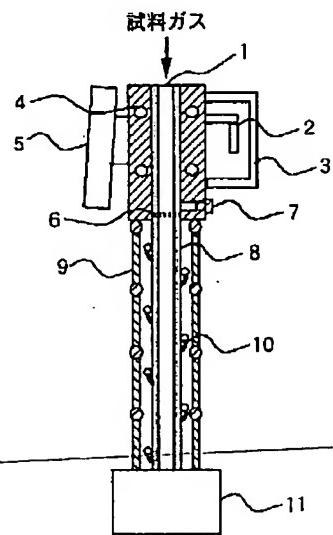
図 1



[Translation done.]

Drawing selection drawing 2

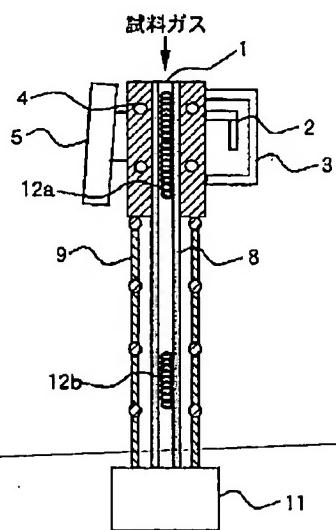
図 2



[Translation done.]

Drawing selection drawing 3

図 3



[Translation done.]